09/914305 JCD3 Recident 70 27 AUG 2001 US 18024

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of: Tiziano Dall'Occo et al. Serial Number: Unknown Filed: August 27, 2001)))		
		US National Phase of International Patent Application No: PCT/EP00/13192)
		Filed: December 22, 2000)
For: PROCESS FOR THE PREPARATION OF ETHYLENE POLYMERS)		

Commissioner for Patents Box Patent Application Washington, D.C. 20231

August 27, 2001

PRELIMINARY AMENDMENT

This is a preliminary amendment to US 18024, filed herewith, which is the US National Phase of the International Patent Application No. PCT/EP00/13192, filed on December 22, 2000, and claiming priority to European Patent Application 99204566.6 filed on December 28, 1999.

In the Specification

Please replace the paragraph beginning at page 2, line 6 and ending at line 10, with the following paragraph:

--A and B are selected from sulfur (S), oxygen (O) and CR^9 , R^9 being selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17

of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹, i.e. either A or B being different from CR⁹;--

Please replace the paragraph beginning at page 26, line 31 and ending at page 27, line 1, with the following paragraph:

--In the copolymers obtainable by the process of the invention, the molar content of ethylene derived units is generally higher than 40%, and preferably it is between 50% and 99%, and more preferably it is between 80% and 98%.--

Please replace the paragraph beginning at page 30, line 20 and ending at page 31, line 1, with the following paragraph:

--A 2.5 M solution of *n*-BuLi in hexane (24.30 mL, 60.76 mmol) was added dropwise at -20°C to a solution of 15.00 g of 2,3-dibromothiophene (Aldrich, 98%, Mw = 241.94, d = 2.137, 60.76 mmol, *n*-BuLi:2,3-Br₂thiophene = 1:1) in 90 mL of ether. The solution turned from pale yellow to yellow. After 1 h stirring at -20°C, 2.53 mL of ethylformate (Aldrich, 97%, Mw = 74.08, d = 0.917, 30.38 mmol, HCOOEt:2,3-Br₂thiophene = 0.5:1) in 30 mL of ether was added dropwise. During the addition the solution turned from yellow to dark yellow. The reaction mixture was kept at -20°C for 15 min, then allowed to warm to room temperature and stirred for 20 h. The final pale orange suspension was poured at 0°C into acidic water (1.65 g of NH₄Cl in 75 mL of water), the organic layer was separated out and the water layer extracted with ether (3 x 25 mL). The organic layers were collected, dried over Na₂SO₄ and the solvents were removed under vacuum at 30-35°C to give an orange oil (9.52 g), which was characterized by GC-MS analysis and ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 32, line 5 and ending at line 26,

with the following paragraph:

-- A 2.5 M solution of n-BuLi in hexane (21.30 mL, 53.25 mmol) was added dropwise at -50°C to a solution of 8.99 g of 3,3'-dibromo-2,2'-dithienylmethane obtained as above described (20741/69A, Mw = 338.09, 26.59 mmol) in 75 mL of ether under nitrogen atmosphere in a 250 mL flask. After 1 h stirring at -50°C, the dark brown dilithium suspension was added slowly to a suspension of 7.26 g of CuCl₂ (Aldrich, 98%, Mw = 134.45, 52.92 mmol) in 50 mL of Et₂O. The reaction mixture was kept at -50°C for 30 min, allowed to warm to-20°C in 2 h 30 min and then allowed to reach 0°C in few minutes. Aliquots were taken after 30 min at -50°C, at -20°C and after 1 h at 0°C to follow the reaction state by GC-MS analysis. It appeared that the CuCl2 induced coupling reaction starts at -50°C but proceeds slowly until 0°C. Only 10% wt. of 7Hcyclopenta[2,1-b:4,3-b']dithiophene was formed after 1h at 0°C. After keeping at 0°C for 1 h 30 min, the reaction mixture was stirred overnight at room temperature and subsequently poured at 0°C into 100 mL of an aqueous 2 M HCl solution. The resulting mixture was stirred for 15 min at room temperature, filtered in order to remove the greyish precipitate of Cu₂Cl₂, the ether layer was separated out and the aqueous phase extracted with ether. The combined ethereal extracts were washed with HCl 2 M (100 mL), two times with NaHCO3 aq. and finally with ether. The resulting organic phase (final volume = 300 mL) was dried over Na₂SO₄ and the solvents removed in vacuo giving 3.16 g of a dark red oil, which was analysed by GC-MS analysis and ¹H-NMR spectroscopy. The analysis showed the presence of the desired product together with dimers, trimers and tars. The crude product was added of 40 mL of ethanol and stirred for 1 h at room temperature. The yellow-orange extract was concentrated in vacuo at 55°C for 4 h to give a dark orange oil (1.92 g), which crystallized by standing at 0°C overnight.--

Please replace the paragraph beginning at page 37, line 19, and ending at line 26 with the following paragraph:

--To a stirred solution of 44.26g of 2-methyl-4-bromo-thiophene (0.25 mol) in 300 mL of ether, 164 mL of a 1.6 M solution of *n*-BuLi (0.26 mol) was added at -70°C. The resulting solution was kept under stirring at -60 to -70°C for 30 min and then was treated with 27.4 g of dimethylformamide (0.37 mol) in 100 mL of ether. The mixture was allowed to warm to room temperature, then neutralized with 10% aqueous solution of NH₄Cl, washed with 10% aqueous solution of H₃PO₄ and finally with water up to neutral pH. The organic phase was collected, evaporated off and distilled at 110°C/10mmHg. Yield 22.3 g (71%). The title compound was characterized by ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 38, line 2, and ending at line 8 with the following paragraph:

--113 mL of 1.6 M *n*-BuLi solution (0.18 mol) was added to a solution of 31.3 g of 2-methyl-4-bromo-thiophene (0.177 mol) in 150 mL of ether at -70°C under stirring. The resulting solution was kept under stirring at -60 to -70°C for 30 min and then was added of 22.3 g of 2-methyl-4-formyl-thiophene (0.177 mol) in 100 mL of ether. The mixture was allowed to warm to room temperature, then neutralized with 10% aqueous solution of NH₄Cl and washed with water. The organic phase was separated out and evaporated off (crude bis(2-methyl-4-thienyl)methanol or 2,2'-dimethyl-4,4'-dithienyl carbinol).--

Please replace the paragraph beginning at page 38, line 9, and ending at line 15 with the following paragraph:

--A suspension of 35.5 g of AlCl₃ (0.266 mol) in 100 mL of ether was added slowly to a suspension of 10 g of LiAlH₄ (0.266 mol) in 100 mL of ether. The resulting mixture was treated with the solution of the carbinol obtained as above described in 100 mL ether. Then the reaction mixture was refluxed for additional 1 h, cooled up to room temperature and finally added of 100 mL of ethyl acetate. After it was treated with 300 mL of water and 300 mL of ether. The organic phase was collected, washed with water, dried over

MgSO₄ and evaporated off. The residue was distilled at 90 to 110°C/0.5 mmHg. Yield 23.2g (63%).--

Please replace the paragraph beginning at page 41, line 2, and ending at line 7 with the following paragraph:

--A suspension of 1.0g(3.22mmol) of 2,2-(cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane in 20ml ether was treated with 4.1ml (6.5mmol) 1.6M BuLi at -70°C. The mixture was allowed to warm to 0°C and then was treated with 0.75g (3.2mmol) ZrCl₄. The reaction mixture was stirred at reflux within 3h, then the yellow precipitate was filtered, washed twice with ether, dried and then recrystallyzed from CH₂Cl₂. Yield 1.37g (90%).--

Please replace the paragraph beginning at page 41, line 23, and ending at page 42, line 6 with the following paragraph:

--2.3 mL of 1.6 M *n*-BuLi solution (3.7 mmol) was added at -70°C to a suspension of 0.6 g (1.85 mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm to 0°C and then was treated with 0.43 g (1.85 mmol) of ZrCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 0.72 g (80%). The title compound was characterized by ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 42, line 11, and ending at line 17 with the following paragraph:

--2.5 mL of 1.6 M n-BuLi solution (4.0mmol) was added at -70°C to a suspension of

0.65 g (2.0 mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm to 0°C and then was treated with 0.64 g (2.0 mmol) of HfCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 0.48 g (42%). The title compound was characterized by ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 43, line 8, and ending at line 14 with the following paragraph:

--3.75 mL of 1.6 M *n*-BuLi solution (6.0 mmol) was added at -70°C to a suspension of 1.06 g (3.0 mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm to 0°C and then was treated with 0.7 g (3.0 mmol) of ZrCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 1.24 g (80%). The title compound was characterized by ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 44, line 6, and ending at line 12 with the following paragraph:

--3.75 mL of 1.6 M *n*-BuLi solution (6.0 mmol) was added at --70°C to a suspension of 1.11 g (3.0 mmol) of 2,2-(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm to 0°C and treated with 0.7g (3.0 mmol) of ZrCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 1.27g (80%). The title compound was characterized by ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 45, line 10, and ending at line 16 with the following paragraph:

--A solution of 1-methyl-3-phenyl-1,3-cyclopentadiene (15.62 g, 0.1 mol) in 100 mL of ethanol was treated at low temperature with 8.6 mL (0.12 mol) of acetone and 9.7 mL (0.12 mol) of pyrrolidine. The resulting solution was kept below room temperature overnight. Then the reaction mixture was neutralized with a 10 % aq. solution of H₃PO₄, extracted with hexane (3 x 50 mL) and washed with water until neutral pH. The organic phase was separated out, dried over MgSO₄ and concentrated. The residue was distilled at 85°C/10mmHg. Yield 5.89g (30%). The desired title compound was characterized by ¹H-NMR.--

Please replace the paragraph beginning at page 45, line 25, and ending at page 46, line 5 with the following paragraph:

--A suspension of 2.0 g (3.85 mmol) of 2,2-(2-methyl-4-phenyl-1-cyclopentadienyl)-7-(2,5-trimethylsilylcyclopenta[1,2-b:4,3-b']-dithiophene)propane in 50 mL of ether was treated at -70°C with 4.8 mL of a 1.6 M *n*-BuLi solution (7.71 mmol). After the addition, the reaction mixture was allowed to warm to 0°C and added of 0.90 g (3.85 mmol) of ZrCl₄. The resulting mixture was allowed to reach room temperature and stirred overnight. Then the brown precipitate obtained was filtered, washed twice with ether, dried and finally recrystallyzed from CH₂Cl₂. Yield 1.82 g (70%).--

Please replace the paragraph beginning at page 46, line 24, and ending at page 47, line 5 with the following paragraph:

--A solution of 1.05 g (3.22 mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(cyclopenta [1,2-b:4,3-b']-dithiophene)propane in a mixture of 10 mL of ether and 60 mL of hexane

7

was treated with 4.1 mL (6.6 mmol) of a 1.6 M *n*-BuLi solution at -70°C. The mixture was allowed to warm to 0°C and treated with 0.75 g (3.2 mmol) of ZrCl₄. The resulting reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with hexane, dried and finally recrystallized from CH₂Cl₂/hexane. Yield 0.32 g (21%). The title compound was characterized by ¹H-NMR spectroscopy.--

Please replace the paragraph beginning at page 49, line 4, and ending at line 10 with the following paragraph:

--A suspension of 1.11 g (3 mmol) of 2,2-(2-methyl-4-isopropyl-1-cyclopentadienyl)-7-{(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']dithiophene)} propane in 10 mL of ether and 50 mL of hexane was treated at -70°C with 3.8 mL of a 1.6 M n-BuLi solution (6.1 mmol). After the addition, the reaction mixture was allowed to warm to 0°C and added of 0.75 g (3.2 mmol) of ZrCl₄. The resulting mixture was allowed to reach room temperature and stirred overnight. Then the yellow precipitate obtained was filtered, washed twice with ether, dried and finally recrystallyzed from CH₂Cl₂.--

In the Claims

Please amend claims 1-4, 6-8, 10, 13, and 15-26 to read as follows:

- --1. (Amended) A process for the preparation of polymers of ethylene comprising the polymerization reaction of ethylene and optionally one or more olefins in the presence of a catalyst comprising the product obtained by contacting:
 - (A) a metallocene compound of formula (I):

$$R^3$$
 R^2
 R^4
 R^5
 R^1
 R^6
 R^6
 R^7
 R^8
 R^8

wherein

the rings containing A and B have a double bond in the allowed position having an aromatic character;

A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_20 -alkyl, C_3 - C_20 -cycloalkyl, C_2 - C_20 -alkenyl, C_6 - C_20 -aryl, C_7 - C_20 -alkylaryl, or C_7 - C_20 -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 ;

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

M is an atom of a transition metal selected from group 3, 4, 5, 6 or the lanthanide or actinide groups in the Periodic Table of the Elements,

X, which may be the same as or different from each other, is hydogen, halogen atom, a R^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10}_2 or PR^{10}_2 group, wherein the substituents R^{10} are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; p is an integer of from 1 to 3, being equal to the oxidation state of the metal M minus 2;

9

with the proviso that said metallocene compound is different from: isopropylidene(cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride; and

- (B) at least one of an alumoxane and a compound capable of forming an alkyl metallocene cation.
- 2. (Amended) The process according to claim 1, wherein in the metallocene compound of formula (I) the transition metal M is selected from titanium, zirconium or hafnium.
- 3. (Amended) The process according to claim 1, wherein in the metallocene compound of formula (I) the X substituents are chlorine atoms or methyl groups.
- 4. (Amended) The process according to claim 1, wherein in the metallocene compound of formula (I) A and B are sulfur or a CH group, either A or B being different from CH, R⁵ and R⁶ are C₁-C₂₀-alkyl groups, and R⁷ is equal to R⁸.
- 6. (Amended) The process according to claim 1, wherein said alumoxane is obtained by contacting water with an organo-aluminium compound of formula $H_jAlR^{12}_{3-j}$ or $H_jAl_2R^{12}_{6-j}$, where R^{12} substituents, same or different, are hydrogen atoms, C_1 - C_{20} -alkyl, C_3 - C_{20} -cyclalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl, optionally containing silicon or germanium atoms with the proviso that at least one R^{12} is different from halogen, and j ranges from 0 to 1, being also a non-integer number.
- 7. (Amended) The process according to claim 6, wherein said alumoxane is methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) or tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).
- 8. (Amended) The process according to claim 1, wherein the compound capable of forming a metallocene alkyl cation is a compound of formula D⁺E⁻, wherein D⁺ is a Brønsted acid, able to give a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E⁻ is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be removed by an olefinic monomer.
- 10. (Amended) The process according to claim 1, wherein the process is carried out

in the presence of an alpha-olefin selected from propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene or 1-dodecene.

- 13. (Amended) The process according to claim 1, wherein the process is carried out in the presence of a cyclic comonomer.
- 15. (Amended) The process according to claim 13, wherein the molar content of the cyclic comonomer is between 0 mol% and 30 mol%.
- 16. (Amended) A process for the preparation of a ligand of formula (II):

$$R^4$$
 R^5
 R^6
 R^1
 R^7
 R^8
(II)

or its double bond isomers,

wherein

A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 ;

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

comprising the following steps:

i) treating the compound of formula (III) with at least one equivalent of a base;

$$R^7$$
 B
 R^8
(III)

wherein the rings containing A and B have a double bond in the allowed position having an aromatic character;

wherein A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 ;

 R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

ii) contacting the thus obtained corresponding anionic compound from step i) with a compound of formula (TV):

$$R^4$$
 R^5
 R^1
 R^1
 R^2
 R^3
 R^4
 R^2

wherein

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents; and

12

- iii) treating the thus obtained product from step ii) with a protonating agent.
- 17. (Amended) The process for the preparation of a ligand of formula (II) according to claim 16 wherein the base used in step i) is selected from hydroxides, hydrides of alkali- and earth-alkali metals, metallic sodium, potassium or organometallic lithium salts, and the protonating agent used in step iii) is a quaternary ammonium salt.
- 18. (Amended) A process for preparing the compound of formula VII

$$R^7$$
 R^9
 R^9
 R^9
(VII)

wherein A is sulfur (S) or oxygen (O), R^9 is hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

 R^7 and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

comprising the following steps:

i) treating a compound of formula (V):

$$R^7$$
 R^9
 R^9
 R^9

13

(V)

wherein A is sulfur or oxygen, with a compound of formula (VI):

wherein A is sulfur or oxygen;

- ii) contacting the thus obtained product from step i) with a reducing agent in a molar ratio between said reducing agent and the product obtained under i) of at least 1;
- iii) contacting the product obtained under ii) with a compound selected from an organolithium compound, sodium or potassium in a molar ratio between said compound and the product obtained in step ii) of equal to or greater than 2; and
- iv) treating the thus obtained product under step iii) with an agent selected from copper chloride, iodine or Mg/Pd, in order to obtain a compound of general formula (VII)
- 19. (Amended) A process for preparing the compound of formula (X)

$$R^9$$
 R^9
 R^9
 R^8
 R^8

wherein B is sulfur or oxygen and R^9 is hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of

the Elements;

R⁷ and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

comprising the following steps:

i) contacting a compound of formula (VIII):

wherein B is sulfur or oxygen,

with a compound of formula (IX):

$$H \stackrel{O}{\stackrel{\parallel}{\subset}}_{R^9}$$

$$(IX)$$

wherein B is sulfur or oxygen,

and subsequently treating with a neutralization agent;

- ii) treating the thus obtained product from step i) with a reducing agent in a molar ratio between said reducing agent and the compound obtained under i) of at least 1;
- iii) contacting the thus obtained product from step ii) with a mixture of an organolithium compound and tetramethylethylenediamine (TMEDA) in a molar ratio between said mixture and the product obtained under ii) of at least 2; and
- iv) contacting the thus obtained product from step iii) with an agent selected from copper chloride, iodine or Mg/Pd, in order to obtain a compound of

formula (X)

20. (Amended) A process for preparing the compound of formula (VII)

$$R^7$$
 R^9
 R^9
 R^9
(VII)

wherein A is sulfur (S) or oxygen (O), R⁹ is hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

 R^7 and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

comprising the following steps:

i) contacting an equimolar mixture of compounds of formulae (XI) and (XII):

wherein A are sulfur or oxygen,

with a Lewis acid or a mixture of a Lewis acid and a protonic acid;

ii) treating the thus obtained product from step i) with CH2O in a molar ratio

between said mixture and CH₂O of a range between 10:1 and 1:10;

- iii) contacting the thus obtained product from step ii) with a compound selected from an organolithium compound, sodium or potassium; and
- iv) contacting the thus obtained product from step iii) with an agent selected from copper chloride, iodine or Mg/Pd, in order to obtain a compound of general formula (VII).
- 21. (Amended) The process according to claim 20, wherein the Lewis acid is selected from zinc dichloride, cadmium dichloride, mercury dichloride, tin tetrachloride, trifluoroborane, zirconium tetrachloride, or titanium tetrachloride.
- 22. (Amended) A process for the preparation of a metallocene compound of the formula (I):

$$R^3$$
 R^2
 R^4
 R^5
 R^1
 R^6
 R^6
 R^7
 R^8
 R^8
 R^8

wherein

the rings containing A and B have a double bond in the allowed position having an aromatic character;

A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 :

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to

groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

with the proviso that said metallocene compound is different from: isopropylidene(cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

comprising the following steps:

a) contacting a compound of formula (II)

$$R^4$$
 R^5
 R^6
 R^1
 R^7
 R^8
(II)

or its double bond isomers,

wherein

A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 :

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent

substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

with a base, wherein the molar ratio between said base and the compound of formula (II) is at least 2;

b) contacting with a compound of formula MX_{p+2},

wherein M is an atom of a transition metal from group 3, 4, 5, 6 or the lanthanide or actinide groups in the Periodic Table of the Elements,

X, which may be the same as or different from each other, is hydogen, halogen atom, a R^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10}_2 or PR^{10}_2 group, wherein the substituents R^{10} are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; and

p is an integer being equal to the oxidation state of the metal M minus 2.

23. (Amended) A process for preparing the compound of formula (VII)

$$R^7$$
 R^9
 R^9
 R^9
(VII)

wherein A is sulfur (S) or oxygen (O), R^9 is hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

 R^7 and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; comprising the following steps:

i) contacting a compound of formula (XIII):

with a base selected from an organolithium compound, sodium or potassium; treating with a formic ester, wherein the molar ratio between said ester and the compound of formula (XIII) is at least 1:2, and subsequently treating the obtained product with a reducing agent in order to obtain a compound of formula (XIV):

ii) contacting the compound of formula (XIV) with a base selected from an organolithium compound, sodium or potassium and subsequently treating the dimetallated compound with an alkylating agent to obtain the compound of formula (XV);

$$R^{9}$$
 Br Br R^{9} R^{9} R^{8} R^{8}

and

iii) contacting the alkylated compound obtained by step ii) with a coupling agent selected from copper chloride, iodine or Mg/Pd in order to obtain the compound of formula (VII).

24. (Amended) A compound of formula (III)

$$R^7$$
 B
 R^8
(III)

wherein the rings containing A and B have a double bond in the allowed position having an aromatic character; A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹;

and R^7 , and R^8 which may be the same as or different from each other, are a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements.

25. (Amended) A metallocene compound of formula (I):

$$R^3$$
 R^2
 R^4
 R^5
 R^6
 R^6
 R^7
 R^8
 R^8
 R^8

wherein

A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 ;

21

R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R¹ and R², R³ and R⁴, or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

M is an atom of a transition metal from group 3, 4, 5, 6 or the lanthanide or actinide groups in the Periodic Table of the Elements,

X, which may be the same as or different from each other, is hydogen, halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰, NR¹⁰₂ or PR¹⁰₂ group, wherein the substituents R¹⁰ are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; p is an integer of from 1 to 3, being equal to the oxidation state of the metal M minus 2;

with the proviso that said metallocene compound is different from:

isopropylidene(cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride, isopropylidene(3-methyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-ethyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-t-butyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-n-butyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-trimethylsilyl-cyclopentadienyl)-7-(

cyclopentadithiophene)zirconium dichloride and

isopropylidene (3-i-propylcyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride.

26. (Amended) A ligand of formula (II):

$$R^4$$
 R^5
 R^6
 R^1
 R^7
 R^8
(II)

or its double bond isomers,

wherein the rings containing A and B have double bonds in any of the allowed positions, having an aromatic character and

A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹; R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R¹ and R², R³ and R⁴, or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

with the proviso that said ligands are different from: isopropylidene(cyclopentadiene)-7-(cyclopentadithiophene), isopropylidene(3-methyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-ethyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-t-butyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-n-butyl-cyclopentadiene)-7-(cyclopentadithiophene); isopropylidene(3-trimethylsilyl-cyclopentadiene)-7-(cyclopentadithiophene) and isopropylidene (3-i-propylcyclopentadiene)-7-(cyclopentadithiophene).--

Please add the following new claim 27:

--27 (New) A process for preparing the compound of formula (VII)

$$R^7$$
 R^9
 R^9
 R^9
(VII)

wherein A is sulfur (S) or oxygen (O), R^9 is hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

 R^7 and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

comprising the following steps:

i) contacting a compound of formula (XIII):

(XIII)

with a base selected from an organolithium compound, sodium or potassium; treating with a formic ester, wherein the molar ratio between said ester and the compound of formula (XIII) is at least 1:2, and subsequently treating the obtained product with a reducing agent in order to obtain a compound of formula (XIV):

ii) contacting the compound of formula (XIV) with a base selected from an organolithium compound, sodium or potassium and subsequently treating the dimetallated compound with an ester of boric acid and a protonating agent in order to obtain the compound of formula (XVI):

$$(HO)_2B$$

Br Br

 R^9
 A
 $B(OH)_2$

(XVI)

and subsequently contacting with a mixture of an alkylating agent in the presence of an transition metal complex compound for obtaining the compound of formula (XV);

$$R^{9}$$
 Br Br R^{9} R^{9} R^{7} A R^{9} R^{9}

and

iii) contacting the alkylated compound obtained by step ii) with a coupling agent

selected from copper chloride, iodine or Mg/Pd in order to obtain the compound of formula (VII).--

REMARKS

This preliminary amendment is being filed concurrently with Applicants' application US 18024, for which a serial number has not yet been assigned.

Typographical errors in the specification have been corrected, and claims 1-4, 6-8, 10, 13, and 15-26 have been amended to better point out and more specifically claim the present invention. New claim 27 has been added, support for which can be found in claim 23 as originally filed. No new matter has been added by these amendments and they do not affect the scope of the claims as originally filed.

Separate pages with a marked-up version of the amended specification and claims entitled: "Version with Markings to Show Changes Made" are attached.

An early and favorable action on the merits is requested. The Applicants invite the Examiner to direct any questions or comments to the undersigned at the telephone number given below.

It is not believed that any fee is required for entry and consideration of this Amendment; nevertheless, the Commissioner is hereby authorized to charge U.S. PTO Deposit Account 08-2336 in the amount of any such required fee.

Respectfully submitted,

William Allen

William R. Reid

Registration No. 47,894 Attorney for Applicant

I hereby certify that this correspondence is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" in an envelope addressed to: Box PCT, Commissioner for Patents, Washington, DC 20231 on August 27, 2001 with the number of the Express Mail label being

EK794120454US.

Enclosure
Basell USA Inc.
912 Appleton Road
Elkton, MD 21921

Attorney's Telephone No.: 410-996-1783

VERSION WITH MARKINGS TO SHOW CHANGES MADE Filed on August 27, 2001

In the Specification

Paragraph beginning at page 2, line 6 and ending at line 10.

A and B are selected from sulfur (S), oxygen (O) and CR^9 , R^9 being selected from hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is $[CR^5]CR^9$ or if B is S or O, A is $[CR^5]CR^9$, i.e. either A or B being different from CR^9 ;

Paragraph beginning at page 26, line 31 and ending at page 27, line 1. In the copolymers obtainable [byh]by the process of the invention, the molar content of ethylene derived units is generally higher than 40%, and preferably it is between 50% and 99%, and more preferably it is between 80% and 98%.

Paragraph beginning at page 30, line 20 and ending at page 31, line 1.

A 2.5 M solution of *n*-BuLi in hexane (24.30 mL, 60.76 mmol) was added dropwise at – 20°C to a solution of 15.00 g of 2,3-dibromothiophene (Aldrich, 98%, Mw = 241.94, d = 2.137, 60.76 mmol, *n*-BuLi:2,3-Br₂thiophene = 1:1) in 90 mL of ether. The solution turned from pale yellow to yellow. After 1 h stirring at –20°C, 2.53 mL of ethylformate (Aldrich, 97%, Mw = 74.08, d = 0.917, 30.38 mmol, HCOOEt:2,3-Br₂thiophene = 0.5:1) in 30 mL of ether was added dropwise. During the addition the solution turned from yellow to dark yellow. The reaction mixture was kept at –20°C for 15 min, then allowed to warm to room temperature and stirred for 20 h. The final pale orange suspension was poured at 0°C into acidic water (1.65 g of NH₄Cl in 75 mL of water), the organic layer was separated out and the water layer extracted with ether (3 x 25 mL). The organic layers were collected, dried [overNa₂SO₄]over Na₂SO₄ and the solvents were removed under vacuum at 30-35°C to give an orange oil (9.52 g), which was characterized by GC-MS analysis and ¹H-NMR spectroscopy.

ТС5421-002ь 28

Paragraph beginning at page 32, line 5 and ending at line 26.

A 2.5 M solution of n-BuLi in hexane (21.30 mL, 53.25 mmol) was added dropwise at 50°C to a solution of 8.99 g of 3,3'-dibromo-2,2'-dithienylmethane obtained as above described (20741/69A, $M_W = 338.09$, 26.59 mmol) in 75 mL of ether under nitrogen atmosphere in a 250 mL flask. After 1 h stirring at -50°C, the dark brown dilithium suspension was added slowly to a suspension of 7.26 g of CuCl₂ (Aldrich, 98%, Mw = 134.45, 52.92 mmol) in 50 mL of Et₂O. The reaction mixture was kept at -50°C for 30 min, allowed to warm to-20°C in 2 h 30 min and then allowed to reach 0°C in few minutes. Aliquots were taken after 30 min at -50°C, at -20°C and after 1 h at 0°C to follow the reaction state by GC-MS analysis. It appeared that the CuCl2 induced coupling reaction starts at -50°C but proceeds slowly until 0°C. Only 10% wt. of 7H-cyclopenta[2,1-b:4,3b']dithiophene was formed after 1h at 0°C. After keeping at 0°C for 1 h 30 min, the reaction mixture was stirred overnight at room temperature and subsequently poured at 0°C into 100 mL of an aqueous 2 M HCl solution. The resulting mixture was stirred for 15 min at room temperature, filtered in order to remove the [greysh]greyish precipitate of Cu₂Cl₂, the ether layer was separated out and the aqueous phase extracted with ether. The combined ethereal extracts were washed with HCl 2 M (100 mL), two times with NaHCO3 aq. and finally with ether. The resulting organic phase (final volume = 300 mL) was dried [overNa₂SO₄]over Na₂SO₄ and the solvents removed in vacuo giving 3.16 g of a dark red oil, which was analysed by GC-MS analysis and ¹H-NMR spectroscopy. The analysis showed the presence of the desired product together with dimers, trimers and tars. The crude product was added of 40 mL of ethanol and stirred for 1 h at room temperature. The yellow-orange extract was concentrated in vacuo at 55°C for 4 h to give a dark orange oil (1.92 g), which crystallized by standing at 0°C overnight.

Paragraph beginning at page 37, line 19, and ending at line 26.

To a stirred solution of 44.26g of 2-methyl-4-bromo-thiophene (0.25 mol) in 300 mL of ether, 164 mL of a 1.6 M solution of n-BuLi (0.26 mol) was added at -70°C. The resulting solution was kept under stirring at -60 [\div]to -70°C for 30 min and then was treated with 27.4 g of

dimethylformamide (0.37 mol) in 100 mL of ether. The mixture was allowed to warm to room temperature, then neutralized with 10% aqueous solution of NH₄Cl, washed with 10% aqueous solution of H₃PO₄ and finally with water up to neutral pH. The organic phase was collected, evaporated off and distilled at 110°C/10mmHg. Yield 22.3 g (71%). The title compound was characterized by ¹H-NMR spectroscopy.

Paragraph beginning at page 38, line 2, and ending at line 8.

113 mL of 1.6 M n-BuLi solution (0.18 mol) was added to a solution of 31.3 g of 2-methyl-4-bromo-thiophene (0.177 mol) in 150 mL of ether at -70°C under stirring. The resulting solution was kept under stirring at -60 [\div]to -70°C for 30 min and then was added of 22.3 g of 2-methyl-4-formyl-thiophene (0.177 mol) in 100 mL of ether. The mixture was allowed to warm to room temperature, then neutralized with 10% aqueous solution of NH₄Cl and washed with water. The organic phase was separated out and evaporated off (crude bis(2-methyl-4-thienyl)methanol or 2,2'-dimethyl-4,4'-dithienyl carbinol).

Paragraph beginning at page 38, line 9, and ending at line 15.

A suspension of 35.5 g of AlCl₃ (0.266 mol) in 100 mL of ether was added slowly to a suspension of 10 g of LiAlH₄ (0.266 mol) in 100 mL of ether. The resulting mixture was treated with the solution of the carbinol obtained as above described in 100 mL ether. Then the reaction mixture was refluxed for additional 1 h, cooled up to room temperature and finally added of 100 mL of ethyl acetate. After it was treated with 300 mL of water and 300 mL of ether. The organic phase was collected, washed with water, dried over MgSO₄ and evaporated off. The residue was distilled at 90[÷] to 110°C/0.5 mmHg. Yield 23.2g (63%).

Paragraph beginning at page 41, line 2, and ending at line 7.

A suspension of 1.0g(3.22mmol) of 2,2-(cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane in 20ml ether was treated with 4.1ml (6.5mmol) 1.6M BuLi at -70°C. The mixture was allowed to warm [to0°C]to 0°C and then was treated with 0.75g (3.2mmol) ZrCl₄. The reaction mixture was stirred at reflux within 3h, then the yellow

ТС5421-002ь 30

precipitate was filtered, washed twice with ether, dried and then recrystallyzed from CH₂Cl₂. Yield 1.37g (90%).

Paragraph beginning at page 41, line 23, and ending at page 42, line 6.

2.3 mL of 1.6 M *n*-BuLi solution (3.7 mmol) was added at -70°C to a suspension of 0.6 g (1.85 mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm [to0°C]to 0°C and then was treated with 0.43 g (1.85 mmol) of ZrCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 0.72 g (80%). The title compound was characterized by ¹H-NMR spectroscopy.

Paragraph beginning at page 42, line 11, and ending at line 17.

2.5 mL of 1.6 M *n*-BuLi solution (4.0mmol) was added at -70°C to a suspension of 0.65 g (2.0 mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm [to0°C]to 0°C and then was treated with 0.64 g (2.0 mmol) of HfCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 0.48 g (42%). The title compound was characterized by ¹H-NMR spectroscopy.

Paragraph beginning at page 43, line 8, and ending at line 14.

3.75 mL of 1.6 M *n*-BuLi solution (6.0 mmol) was added at -70°C to a suspension of 1.06 g (3.0 mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm [to0°C] to 0°C and then was treated with 0.7 g (3.0 mmol) of ZrCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 1.24 g (80%). The title compound was characterized by ¹H-NMR spectroscopy.

тс5421-002ь 31

Paragraph beginning at page 44, line 6, and ending at line 12.

3.75 mL of 1.6 M *n*-BuLi solution (6.0 mmol) was added at -70°C to a suspension of 1.11 g (3.0 mmol) of 2,2-(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene)propane in 20 mL of ether. The mixture was allowed to warm [to0°C]to 0°C and treated with 0.7g (3.0 mmol) of ZrCl₄. The reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with ether, dried and finally recrystallized from CH₂Cl₂. Yield 1.27g (80%). The title compound was characterized by ¹H-NMR spectroscopy.

Paragraph beginning at page 45, line 10, and ending at line 16.

A solution of 1-methyl-3-phenyl-1,3-cyclopentadiene (15.62 g, 0.1 mol) in 100 mL of ethanol was treated at low temperature with 8.6 mL (0.12 mol) of acetone and 9.7 mL (0.12 mol) of pyrrolidine. The resulting solution was kept below room temperature overnight. Then the reaction mixture was neutralized with a 10 % aq. solution of H₃PO₄, extracted with hexane (3 x 50 mL) and washed with water until neutral pH. The organic phase was separated out, dried [overMgSO₄]over MgSO₄ and concentrated. The residue was distilled at 85°C/10mmHg. Yield 5.89g (30%). The desired title compound was characterized by ¹H-NMR.

Paragraph beginning at page 45, line 25, and ending at page 46, line 5.

A suspension of 2.0 g (3.85 mmol) of 2,2-(2-methyl-4-phenyl-1-cyclopentadienyl)-7-(2,5-trimethylsilylcyclopenta[1,2-b:4,3-b']-dithiophene)propane in 50 mL of ether was treated at –

70°C with 4.8 mL of a 1.6 M *n*-BuLi solution (7.71 mmol). After the addition, the reaction mixture was allowed to warm [to0°C]to 0°C and added of 0.90 g (3.85 mmol) of ZrCl₄. The resulting mixture was allowed to reach room temperature and stirred overnight. Then the brown precipitate obtained was filtered, washed twice with ether, dried and finally recrystallyzed from CH₂Cl₂. Yield 1.82 g (70%).

ТС5421-002ь 32

Paragraph beginning at page 46, line 24, and ending at page 47, line 5.

A solution of 1.05 g (3.22 mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(cyclopenta [1,2-b:4,3-b']-dithiophene)propane in a mixture of 10 mL of ether and 60 mL of hexane was treated with 4.1 mL (6.6 mmol) of a 1.6 M *n*-BuLi solution at –70°C. The mixture was allowed to warm [to0°C]to 0°C and treated with 0.75 g (3.2 mmol) of ZrCl₄. The resulting reaction mixture was refluxed under stirring for 3 h, then the yellow precipitate was filtered, washed twice with hexane, dried and finally recrystallized from CH₂Cl₂/hexane. Yield 0.32 g (21%). The title compound was characterized by ¹H-NMR spectroscopy.

Paragraph beginning at page 49, line 4, and ending at line 10.

A suspension of 1.11 g (3 mmol) of 2,2-(2-methyl-4-isopropyl-1-cyclopentadienyl)-7-\(\frac{1}{2},5\)-dimethyl-cyclopenta[1,2-b:4,3-b']dithiophene)\(\rangle\) propane in 10 mL of ether and 50 mL of hexane was treated at -70°C with 3.8 mL of a 1.6 M n-BuLi solution (6.1 mmol). After the addition, the reaction mixture was allowed to warm [to0°C] \(\frac{1}{2}\to0°C\) and added of 0.75 g (3.2 mmol) of ZrCl₄. The resulting mixture was allowed to reach room temperature and stirred overnight. Then the yellow precipitate obtained was filtered, washed twice with ether, dried and finally recrystallyzed from CH₂Cl₂.

In the Claims

Claims 1-4, 6-8, 10, 13, and 15-26 have been changed by deleting the characters in brackets and adding the underlined material, as reported below. For the Examiner's convenience, even the unchanged claims have been reported in the following.

- 1. (Amended) [a] A process for the preparation of polymers of ethylene comprising the polymerization reaction of ethylene and optionally one or more olefins in the presence of a catalyst comprising the product [obtainable]obtained by contacting:
 - (A) <u>a metallocene compound of formula (I):</u>

$$R^3$$
 R^2
 R^4
 R^5
 R^6
 R^6
 R^7
 R^8
 R^8
 R^8

wherein

the rings containing A and B have a double bond in the allowed position having an aromatic character;

A and B are selected from sulfur (S), oxygen (O) [and]or CR 9 , R 9 being [selected from] hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is [CR 5]CR 9 or if B is S or O, A is [CR 5]CR 9 ; R 1 , R 2 , R 3 , R 4 , R 5 , R 6 , R 7 , and R 8 which may be the same as or different from each other, are [selected from] hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R 1 and R 2 [and/or], R 3 and R 4 , [and/or]or R 5 and R 6 can form a ring comprising 4 to 8 atoms, [which can bear]optionally bearing substituents; M is an atom of a transition metal selected from [those belonging to]group 3, 4, 5, 6 or [to] the lanthanide or actinide groups in the Periodic Table of the Elements[(new IUPAC version)],

X, which may be the same as or different from each other, is hydogen, halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰, NR¹⁰₂ or PR¹⁰₂ group, wherein the substituents R¹⁰ are [selected from]hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; p is an integer of from 1 to 3, being equal to the oxidation state of the metal M minus 2; with the proviso that said metallocene compound is different from:

isopropylidene(cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride[being excluded]; and

- (B) <u>at least one of an alumoxane [and/or] and a compound capable of forming an alkyl metallocene cation.</u>
- 2. (Amended) The process according to claim 1, wherein in the metallocene compound of formula (I) the transition metal M is selected from titanium, zirconium [and]or hafnium.
- 3. (Amended) The process according to [any of claims] claim 1[to 2], wherein in the metallocene compound of formula (I) the X substituents are chlorine atoms or methyl groups.
- 4. (Amended) The process according to [any of claims]claim 1[to 3], wherein in the metallocene compound of formula (I) A and B are [selected from]sulfur [and]or a CH group, either A or B being different from CH, R⁵ and R⁶ are C₁-C₂₀-alkyl groups, and R⁷ is equal to R⁸.
- 5. The process according to claim 4, wherein R^1 , R^3 and R^4 are hydrogen, R^5 and R^6 are methyl, R^2 is C_1 - C_{20} -alkyl groups and R^7 and R^8 are hydrogen or methyl groups.
- 6. (Amended) The process according to [any of claims]claim 1[to 5], wherein said alumoxane is obtained by contacting water with an organo-aluminium compound of formula H_jAlR¹²_{3-j} or H_jAl₂R¹²_{6-j}, where R¹² substituents, same or different, are hydrogen atoms, C₁-C₂₀-alkyl, C₃-C₂₀-cyclalkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl, optionally containing silicon or germanium atoms with the proviso that at least one R¹² is different from halogen, and j ranges from 0 to 1, being also a non-integer number.
- 7. (Amended) The process according to claim 6, wherein said alumoxane is methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) [and]or tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).
- 8. (Amended) The process according to [any of claims]claim 1[to 5], wherein the compound capable of forming a metallocene alkyl cation is a compound of formula D⁺E⁻, wherein D⁺ is a Brønsted acid, able to give a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E⁻ is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be removed by an olefinic

monomer.

- 9. The process according to claim 8, wherein the anion Z comprises one or more boron atoms.
- 10. (Amended) The process according to [any of claims] claim 1[to 9], wherein the process is carried out in the presence of an alpha-olefin selected from propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene [and] or 1-dodecene.
- 11. The process according to claim 10, wherein said alpha-olefin is 1-hexene or propylene.
- 12. The process according to claim 10, wherein the molar content of alpha-olefin derived units is between 0% and 60%.
- 13. (Amended) The process according to [any of claims] claim 1[to 9], wherein the process is carried out in the presence of a cyclic comonomer.
- 14. The process according to claim 13, wherein the cyclic comonomer is 5-ethyliden-2-norbornene.
- 15. (Amended) The process according to [claims]claim 13[or 14], wherein the molar content of the cyclic comonomer is between [0mol%]0 mol% and [30mol%]30 mol%.
- 16. (Amended) A process for the preparation of a ligand of formula (II):

$$R^4$$
 R^5
 R^6
 R^1
 R^7
 R^7
 R^8
(II)

[and/or]or its double bond isomers,

wherein [A, B, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are defined as in claims 1-5,]

A and B are selected from sulfur (S), oxygen (O) or CR^9 , R^9 being hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 ;

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, TC5421-002b 36

are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

comprising the following steps:

i) treating the compound of formula (III) with at least one equivalent of a base;

$$R^7$$
 B
 R^8
(III)

wherein the rings containing A and B have a double bond in the allowed position having an aromatic character; [A, B, R⁷ and R⁸ are defined as in claims 1-5]

wherein A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹;

R⁷, and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

ii) contacting the thus obtained corresponding anionic compound [of formula (III)] from step i) with a compound of formula (IV):

$$R^4$$
 R^5
 R^1

(IV)

wherein $[R^1, R^2, R^3, R^4, R^5$ and R^6 are defined as in claims 1-5,]

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents; and

- iii) treating the thus obtained product from step ii) with a protonating agent.
- 17. (Amended) The process for the preparation of a ligand of formula (II) according to claim 16 wherein [The]the base used in step i) is selected from hydroxides, [and]hydrides of alkali- and earth-alkali metals, metallic sodium[and], potassium [and]or organometallic lithium salts, and the protonating agent used in [the above process]step iii) is a quaternary ammonium salt.
- 18. (Amended) A process for preparing the compound of formula [(III) as defined in claim 16]VII

$$\begin{array}{c|c}
A & A & A \\
\hline
R^9 & R^9 \\
\hline
(VII)
\end{array}$$

wherein A is sulfur (S) or oxygen (O), R⁹ is hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

R⁷ and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-aryl-alkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

[wherein B is a CR⁹ group] comprising the following steps:

i) treating a compound of formula (V):

$$R^7$$
 R^9
 R^9
 R^9
 R^9

wherein A is sulfur or oxygen, with a compound of formula (VI):

wherein A is sulfur or oxygen[,];

- ii) contacting the thus obtained product <u>from step i)</u> with a reducing agent in a molar ratio between said reducing agent and the product obtained under i) of at least 1;
- iii) contacting the product obtained under ii) with a compound selected from an organolithium compound, sodium [and]or potassium in a molar ratio between said compound and the product obtained in step ii) of equal to or greater than 2; and
- treating the thus obtained product <u>under step iii)</u> with an agent selected from [the group consisting of]copper chloride, iodine [and]<u>or Mg/Pd[.]</u>, in order to obtain a compound of general formula (VII)[:

$$R^7$$
 R^9
 R^9
 R^9
(VII)].

19. (Amended) A process for preparing the compound of formula [(III) as defined in claim 16](X)

$$\frac{R^9}{R^7}$$

$$\frac{R^9}{R^8}$$

$$\frac{R^9}{(X)}$$

wherein B is sulfur or oxygen and [A is a CR⁹ group] R⁹ is hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

R⁷ and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-aryl-alkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

comprising the following steps:

[v] <u>i)</u> contacting a compound of formula (VIII):

wherein B is sulfur or oxygen, with a compound of formula (IX):

wherein B is sulfur or oxygen, and subsequently treating with a neutralization agent;

[vi)] ii) treating the thus obtained product from step i) with a reducing agent in a molar

ratio between said reducing agent and the compound obtained under i) of at least 1;

- [vii)] iii) contacting the thus obtained product from step ii) with a mixture of an organolithium compound and tetramethylethylenediamine (TMEDA) in a molar ratio between said mixture and the product obtained under ii) of at least 2[,]; and
- [viii)] iv) contacting the thus obtained product from step iii) with an agent selected from [the group consisting of]copper chloride, iodine [and]or Mg/Pd[.], in order to obtain a compound of formula (X)[:

$$R^9$$
 R^9
 R^8
 R^8

20. (Amended) A process for preparing the compound of formula [(III) as defined in claim 16](VII)

$$R^7$$
 R^9
 R^9
 R^9

wherein A is sulfur (S) or oxygen (O), R⁹ is hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

R⁷ and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-aryl-alkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

[wherein A is sulfur or oxygen and B is a CR9 group]comprising the following steps:

i) contacting an equimolar mixture of compounds of formulae (XI) and (XII):

$$Br$$
 R^9
 R^8
 R^7
 R^9
 R^9

wherein A are sulfur or oxygen,

with a Lewis acid or a mixture of a Lewis acid and a protonic acid;

- treating the thus obtained product <u>from step i)</u> with CH₂O in a molar ratio between said mixture and CH₂O of a range between 10:1 and 1:10;
- iii) contacting the thus obtained product <u>from step ii)</u> with a compound selected from an organolithium compound, sodium [and]<u>or</u> potassium; <u>and</u>
- iv) contacting the thus obtained product <u>from step iii)</u> with an agent selected from [the group consisting of]copper chloride, iodine [and]<u>or Mg/Pd[.]</u>, in order to obtain a compound of general formula (VII).
- 21. (Amended) The process according to claim 20, wherein the Lewis acid is selected from zinc dichloride, cadmium dichloride, mercury dichloride, tin tetrachloride, trifluoroborane, zirconium tetrachloride, or titanium tetrachloride.
- 22. (Amended) A process for the preparation of a metallocene compound of the formula

$$R^3$$
 R^2
 R^4
 R^5
 R^5
 R^6
 R^6
 R^7
 R^8
 R^8
 R^8

wherein

(I):

the rings containing A and B have a double bond in the allowed position having an aromatic character;

A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹;

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

with the proviso that said metallocene compound is different from: isopropylidene(cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride;

comprising the following steps:

a) contacting a compound of formula (II) [as defined in claim 16]

$$\begin{array}{c|c}
R^4 & R^3 \\
R^5 & R^1 \\
\hline
R^7 & B & R^8 \\
\hline
(II)
\end{array}$$

or its double bond isomers.

wherein

A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or

 $\underline{C_7}$ - $\underline{C_{20}}$ -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR^9 or if B is S or O, A is CR^9 ;

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R^1 and R^2 , R^3 and R^4 , or R^5 and R^6 can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

with a base, wherein the molar ratio between said base and the compound of formula (II) is at least 2;

b) contacting with a compound of formula MX_{p+2} , [M and X being defined as in claim 1]

wherein M is an atom of a transition metal from group 3, 4, 5, 6 or the lanthanide or actinide groups in the Periodic Table of the Elements,

X, which may be the same as or different from each other, is hydogen, halogen atom, a R^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10} , OR^{10} , OR^{10} , OSO_2CF_3 , $OCOR^{10}$, SR^{10} , NR^{10} , OR^{10} , $OR^{$

p is an integer being equal to the oxidation state of the metal M minus 2.

23. (Amended) A process for preparing the compound of formula [(III) as defined in claim 16](VII)

$$\begin{array}{c|c}
A & A & A \\
\hline
R^7 & R^9 & R^9
\end{array}$$

$$\begin{array}{c|c}
\hline
(VII) & \\
\end{array}$$

wherein A is sulfur (S) or oxygen (O). R⁹ is hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing

heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

R⁷ and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-aryl-alkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

[wherein A is sulfur or oxygen and B is a CR⁹ group]comprising the following steps:

i) contacting a compound of formula (XIII):

with a base selected from an organolithium compound, sodium or potassium; treating with a formic ester, wherein the molar ratio between said ester and the compound of formula (XIII) is at least 1:2, and subsequently treating the obtained product with a reducing agent in order to obtain a compound of formula (XIV):

contacting the compound of formula (XIV) with a base selected from an organolithium compound, sodium or potassium and subsequently treating the dimetallated compound with an alkylating agent to obtain the compound of formula (XV);

$$R^{9}$$
 Br Br R^{9} R^{9} R^{8} R^{8}

[or alternatively treating the dimetallated compound with an ester of boric acid and a protonating agent in order to obtain the compound of formula (XVI):

$$(HO)_2B$$

Br Br

 R^9
 A
 $B(OH)_2$
 (XVI)

and subsequently contacting with a mixture of an alkylating agent in the presence of an transition metal complex compound for obtaining the compound of formula (XV);]and

- iii) contacting the alkylated compound obtained by step [b)]ii) with a coupling [agent;]agent selected from [the group consisting of]copper chloride, iodine [and]or Mg/Pd in order to obtain the compound of formula (VII).
- 24. (Amended) A compound of formula (III)

$$R^7$$
 B
 R^8
(III)

wherein the rings containing A and B have a double bond in the allowed position having an aromatic character; A and B are [described in claims 1-5] selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹;

and R^7 , and R^8 which may be the same as or different from each other, are [selected from] a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl, or C_7 - C_{20} -arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements.

25. (Amended) A metallocene compound of formula (I):

$$R^3$$
 R^2
 R^4
 R^5
 R^1
 R^6
 R^6
 R^7
 R^8
 R^8

wherein [A, B, M, X, p, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, and R⁹ have the meaning as in claims 1-5;]

A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹;

R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R¹ and R², R³ and R⁴, or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

M is an atom of a transition metal from group 3, 4, 5, 6 or the lanthanide or actinide groups in the Periodic Table of the Elements,

X, which may be the same as or different from each other, is hydogen, halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰, NR¹⁰₂ or PR¹⁰₂ group, wherein the substituents R¹⁰ are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements; p is an integer of from 1 to 3, being equal to the oxidation state of the metal M minus 2; with the proviso that said metallocene compound is different from:

isopropylidene(cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride, isopropylidene(3-methyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-ethyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-t-butyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-n-butyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride;

isopropylidene(3-trimethylsilyl-cyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride and

isopropylidene (3-i-propylcyclopentadienyl)-7-(cyclopentadithiophene)zirconium dichloride[being excluded].

26. (Amended) [a]A ligand of formula (II):

$$R^4$$
 R^5
 R^6
 R^1
 R^7
 R^7
 R^8
(II)

[and/or]or its double bond isomers,

wherein the rings containing A and B have double bonds in any of the allowed [position]positions, having an aromatic character and [A, B, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ have the meaning as in claims 1-5;]

A and B are selected from sulfur (S), oxygen (O) or CR⁹, R⁹ being hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, with the proviso that if A is S or O, B is CR⁹ or if B is S or O, A is CR⁹;

 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 which may be the same as or different from each other, are hydrogen, a C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl,

C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements, and at least two adjacent substituents R¹ and R², R³ and R⁴, or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, optionally bearing substituents;

with the proviso that said ligands are different from:

isopropylidene(cyclopentadiene)-7-(cyclopentadithiophene),

isopropylidene(3-methyl-cyclopentadiene)-7-(cyclopentadithiophene);

isopropylidene(3-ethyl-cyclopentadiene)-7-(cyclopentadithiophene);

isopropylidene(3-t-butyl-cyclopentadiene)-7-(cyclopentadithiophene);

isopropylidene(3-n-butyl-cyclopentadiene)-7-(cyclopentadithiophene);

isopropylidene(3-trimethylsilyl-cyclopentadiene)-7-(cyclopentadithiophene) and isopropylidene (3-i-propylcyclopentadiene)-7-(cyclopentadithiophene)[being

excluded].

(New) A process for preparing the compound of formula (VII)

$$\begin{array}{c|c}
A & A & A \\
\hline
R^7 & R^9 & R^9
\end{array}$$

$$\begin{array}{c}
(VII) & \\
\end{array}$$

wherein A is sulfur (S) or oxygen (O), R⁹ is hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

R⁷ and R⁸ which may be the same as or different from each other, are hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, or C₇-C₂₀-arylalkyl radical, optionally containing heteroatoms belonging to groups 13 or 15-17 of the Periodic Table of the Elements;

ž

comprising the following steps:

i) contacting a compound of formula (XIII):

with a base selected from an organolithium compound, sodium or potassium; treating with a formic ester, wherein the molar ratio between said ester and the compound of formula (XIII) is at least 1:2, and subsequently treating the obtained product with a reducing agent in order to obtain a compound of formula (XIV):

ii) contacting the compound of formula (XIV) with a base selected from an organolithium compound, sodium or potassium and subsequently treating the dimetallated compound with an ester of boric acid and a protonating agent in order to obtain the compound of formula (XVI):

$$\begin{array}{c|c}
R^9 & \text{Br Br} & R^9 \\
\hline
(HO)_2B & A & B(OH)_2
\end{array}$$

$$\begin{array}{c|c}
(XVI) & & & \\
\hline
(XVI) & & & \\
\end{array}$$

and subsequently contacting with a mixture of an alkylating agent in the presence of an transition metal complex compound for obtaining the compound of formula (XV):

$$\frac{R^{9} \quad \text{Br Br} \quad R^{9}}{\frac{(XV)}{}}$$

<u>and</u>

iii) contacting the alkylated compound obtained by step ii) with a coupling agent selected from copper chloride, iodine or Mg/Pd in order to obtain the compound of formula (VII).